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References

ANDERSEN, R. A. (1979). *Inorg. Chem.* **18**, 1507–1509.
BRENNAN, J., SHINOMOTO, R., ZALKIN, A. & EDELSTEIN, N. (1984). *Inorg. Chem.* **23**, 4143–4146.
BURNS, J. H. & BALDWIN, W. H. (1976). *J. Organomet. Chem.* **120**, 361–367.
DUTTERA, M. R., FAGAN, P. J., MARKS, T. J. & DAY, V. W. (1982). *J. Am. Chem. Soc.* **104**, 865–867.
International Tables for X-ray Crystallography (1974). Vol. IV. Table 2.2, pp. 71–102. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
ROGERS, R. D., ATWOOD, J. L., EMAD, A., SIKORA, D. J. & RAUCH, M. D. (1981). *J. Organomet. Chem.* **216**, 383–392.
ROGERS, R. D., BYNUM, R. V. & ATWOOD, J. L. (1980). *J. Organomet. Chem.* **192**, 65–73.
WASER, J. (1963). *Acta Cryst.* **16**, 1091–1094.
WASSERMAN, H. J., MOODY, D. C. & RYAN, R. R. (1984). *J. Chem. Soc. Chem. Commun.* pp. 532–533.
WASSERMAN, H. J., ZOZULIN, A. J., MOODY, D. C., RYAN, R. R. & SALAZAR, K. V. (1983). *J. Organomet. Chem.* **254**, 305–311.

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Structure of Tetrakis[2(1*H*)-pyridinethione-*S*]copper(I) Perchlorate–2-Pyridinethione (1/2), $[Cu(C_5H_5NS)_4]ClO_4.2(C_5H_5NS)$

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Abstract. $M_r = 830{\cdot}0$, triclinic, $P\bar{1}$, $a = 10{\cdot}269\ (1)$, $b = 11{\cdot}988\ (1)$, $c = 15{\cdot}982\ (2)$ Å, $\alpha = 95{\cdot}19\ (1)$, $\beta = 106{\cdot}53\ (2)$, $\gamma = 101{\cdot}23\ (1)°$, $V = 1827{\cdot}6$ Å^3, $Z = 2$, $D_x = 1{\cdot}508$, $D_m = 1{\cdot}495$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}0244$ mm^{-1}, $F(000) = 852$, room temperature, final $R = 0{\cdot}048$ for 2150 independent non-zero reflexions. The structure consists of isolated $Cu(C_5H_5NS)_4^+$ ions connected to the ClO_4^- ions through N—H···O hydrogen bonds. The non-coordinated 2-pyridinethione molecules are also connected to the ions through N—H···O hydrogen bonds. The Cu atom in the complex ion is surrounded by four S atoms in a distorted tetrahedral coordination, Cu—S range 2·273 (3)–2·480 (3) Å.

Introduction. Metal complexes of 2-pyridinethiol have attracted considerable attention mainly because of their relevance to certain biological systems (Evans & Wilkinson, 1974; Cotton, Fanwick & Fitch, 1978) and, to a lesser extent, due to the ability of 2-pyridinethiol to act as a uni- or bidentate or as a bridging ligand (Fletcher & Skapski, 1972). Of particular interest are complexes of Cu$^{\text{I}}$ since the stereochemistry of this metal with soft ligands is very flexible. We report here the crystal structure of the title complex, TPTCP. Magnetic measurements, showing the compound to be diamagnetic, indicated that copper is in the +1 oxidation state.

Experimental. Yellow crystals prepared by treating copper perchlorate with 2-pyridinethiol in alcohol solution, m.p. 403 K, D_m measured by flotation in CCl_4/CH_2Cl_2, measured crystal $0{\cdot}55 \times 0{\cdot}43 \times 0{\cdot}15$ mm, Philips PW 1100 computer-controlled four-circle single-crystal diffractometer, cell parameters and standard deviation by least-squares analysis of measured θ angles of the 25 strongest reflexions, intensity statistics indicated $P\bar{1}$, Nb-filtered Mo $K\alpha$, ω–2θ scan, scan width $\Delta\omega = (1{\cdot}0{+}0{\cdot}35\tan\theta)°$, three standard reflexions without significant intensity variation, 3425 reflexions measured, $\theta = 2$–$20°$ (max. *hkl* range $= \pm 9$, ± 11, 15), 2150 unique reflections with $I > 2\sigma(I)$, no absorption correction; direct methods with *MULTAN*77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977), 29 non-H atoms located on *E*

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map, remainder from Fourier synthesis, full-matrix least-squares refinement with *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), anisotropic thermal parameters, atomic scattering factors and anomalous-dispersion corrections for Cu and S from *International Tables for X-ray Crystallography* (1974), H atoms at calculated positions, 24 of them refined, $U_{\rm iso}$ as those of bonded atoms and not refined, $\sum w(|F_o|-|F_c|)^2$ minimized, $w^{-1}=\sigma^2(F_o)+0{\cdot}0002F_o^2$; $R=0{\cdot}048$, $wR=0{\cdot}044$, $S=1{\cdot}12$, max. $\Delta/\sigma=1{\cdot}16$, average $\Delta/\sigma=0{\cdot}15$ (0·57 and 0·11 respectively if H atoms excluded), max. and min. $\Delta\rho$ excursions in final difference Fourier map 0·64 and −0·69 e Å^{-3}.

Discussion. The final positional parameters and equivalent isotropic temperature coefficients for the non-H atoms are given in Table 1.* Interatomic distances and angles are given in Table 2. A clinographic projection of the asymmetric unit, with atom labelling, is shown in Fig. 1. In the $\mathrm{Cu(C_5H_5NS)_4^+}$ ion the Cu atom is surrounded by the four S atoms in a distorted tetrahedral coordination. As in the case of tetrakis(2-imidazolidinethionato)copper(I) nitrate (Battaglia, Corradi, Nardelli & Vidoni Tani, 1976), three of the S—Cu—S bond angles are nearly those of a regular tetrahedron while the rest deviate considerably from 109°. The Cu—S bond lengths are not all equal, range 2·273 (3)–2·480 (3) Å. Their mean value 2·351 (3) Å, however, is comparable with the sum of the corresponding tetrahedral radii, *i.e.* 2·39 Å (Pauling, 1960).

S(3) and S(4), which are involved in the two longer Cu—S distances, take part also, respectively, in two and in one hydrogen-bridging bonds (Table 2 and Fig. 2). A similar inequality of Cu—S distances was reported for tris(thiourea)copper(I) chloride (Okaya & Knobler, 1964) where, however, the two longer Cu—S distances are those for S atoms bonded to two Cu atoms. Compared with the corresponding bonds involving trigonal Cu in tris[2(1*H*)-pyridinethione-*S*]copper(I) nitrate (Kokkou, Fortier, Rentzeperis & Karagiannidis, 1983), the Cu—S distances are significantly longer.

The S—C bond distances are normal and the Cu—S—C bond angles fall within the range of values so far reported (Kokkou *et al.*, 1983, and literature cited therein).

The geometrical features of the pyridine rings, both in $\mathrm{Cu(C_5H_5NS)_4^+}$ ions and in the non-coordinated 2-pyridinethione molecules are close to those of an aromatic ring. The mean C—C and C—N distances in rings *P*1, *P*2, *P*3, *P*4, *P*5 and *P*6 are 1·37 (1) and

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å^2) *for the non*-H *atoms*

$B_{\rm eq}=\frac{8}{3}\pi^2$ trace $\mathbf{\tilde{U}}$.

Here and throughout this paper e.s.d.'s are given in parentheses and refer to the last digit.

	x	*y*	*z*	$B_{\rm eq}$
Cu	0·4511 (1)	0·7505 (1)	0·5680 (1)	3·9
S(1)	0·5920 (2)	0·6885 (2)	0·4956 (1)	4·4
S(2)	0·3321 (3)	0·8865 (2)	0·5223 (2)	4·8
S(3)	0·2773 (2)	0·5789 (2)	0·5748 (1)	3·6
S(4)	0·5803 (2)	0·7701 (2)	0·7194 (1)	3·6
Cl	0·1954 (3)	0·3150 (2)	−0·0022 (2)	4·3
O(1)	0·3093 (6)	0·3925 (6)	0·0648 (4)	6·3
O(2)	0·2375 (7)	0·2924 (7)	−0·0774 (5)	8·7
O(3)	0·0816 (6)	0·3691 (5)	−0·0243 (4)	5·4
O(4)	0·1559 (9)	0·2136 (7)	0·0282 (5)	9·6
C(1)	0·5471 (8)	0·6978 (7)	0·3855 (6)	3·1
C(2)	0·4600 (9)	0·7637 (8)	0·3404 (6)	4·3
C(3)	0·4328 (10)	0·7640 (8)	0·2531 (7)	4·8
C(4)	0·4958 (10)	0·7007 (9)	0·2049 (6)	5·2
C(5)	0·5783 (10)	0·6366 (9)	0·2467 (6)	5·7
N(1)	0·6050 (7)	0·6379 (6)	0·3354 (5)	4·1
C(6)	0·2972 (9)	0·9523 (7)	0·6103 (7)	4·0
C(7)	0·2096 (10)	1·0311 (9)	0·6003 (7)	7·1
C(8)	0·1873 (13)	1·0790 (10)	0·6735 (11)	9·0
C(9)	0·2463 (15)	1·0569 (11)	0·7578 (11)	9·3
C(10)	0·3361 (11)	0·9848 (9)	0·7685 (7)	6·1
N(2)	0·3563 (8)	0·9338 (6)	0·6932 (6)	4·5
C(11)	0·1705 (9)	0·6414 (7)	0·6185 (6)	3·0
C(12)	0·1833 (10)	0·6604 (8)	0·7085 (6)	4·3
C(13)	0·0924 (12)	0·7145 (9)	0·7368 (7)	5·3
C(14)	−0·0091 (11)	0·7547 (9)	0·6773 (9)	5·6
C(15)	−0·0218 (10)	0·7339 (9)	0·5902 (8)	5·2
N(3)	0·0679 (8)	0·6812 (6)	0·5646 (4)	3·8
C(16)	0·7133 (8)	0·8899 (7)	0·7428 (5)	3·1
C(17)	0·7281 (9)	0·9714 (8)	0·6865 (6)	4·0
C(18)	0·8367 (10)	1·0664 (9)	0·7120 (7)	4·6
C(19)	0·9334 (11)	1·0853 (9)	0·7960 (8)	5·0
C(20)	0·9196 (11)	1·0051 (12)	0·8490 (7)	5·2
N(4)	0·8131 (8)	0·9098 (7)	0·8229 (4)	3·9
S(5)	−0·0300 (2)	0·6631 (2)	0·3530 (1)	4·2
C(21)	0·0688 (8)	0·5934 (7)	0·3084 (6)	3·3
C(22)	0·0546 (10)	0·5750 (8)	0·2175 (6)	4·5
C(23)	0·1336 (10)	0·5160 (8)	0·1858 (6)	4·5
C(24)	0·2369 (10)	0·4728 (8)	0·2433 (6)	4·5
C(25)	0·2533 (10)	0·4910 (8)	0·3308 (7)	4·0
N(5)	0·1718 (7)	0·5514 (6)	0·3611 (4)	3·2
S(6)	0·7001 (3)	0·0141 (3)	−0·0154 (3)	9·7
C(26)	0·6885 (11)	0·1504 (9)	0·0053 (6)	4·7
C(27)	0·7897 (11)	0·2483 (11)	0·0050 (7)	4·5
C(28)	0·7790 (13)	0·3555 (10)	0·0259 (7)	4·5
C(29)	0·6651 (14)	0·3764 (10)	0·0521 (7)	4·9
C(30)	0·5666 (12)	0·2825 (11)	0·0542 (7)	4·6
N(6)	0·5779 (8)	0·1741 (7)	0·0290 (5)	4·5

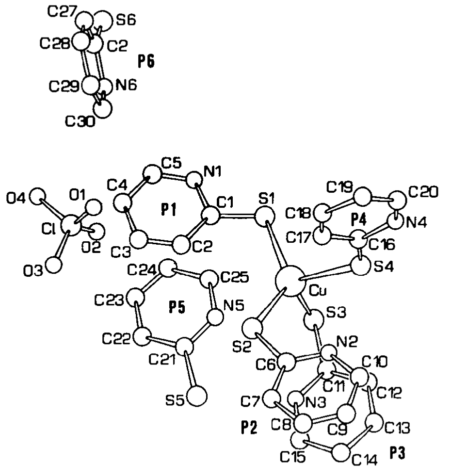

Fig. 1. Clinographic projection of the TPTCP molecule.

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* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters and least-squares-planes' calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42146 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1·36 (1), 1·38 (2) and 1·37 (2), 1·39 (2) and 1·35 (2), 1·38 (1) and 1·36 (1), 1·38 (2) and 1·36 (1), and 1·38 (2) and 1·37 (2) Å. These values and the corresponding bond angles are in agreement with the values found in most pyridine compounds (Kokkou *et al.*, 1983).

Table 2. *Interatomic distances* (Å) *and angles* (°)

Cu–S(1)	2·282 (3)	Cl–O(1)	1·436 (6)
Cu–S(2)	2·273 (3)	Cl–O(2)	1·410 (9)
Cu–S(3)	2·480 (3)	Cl–O(3)	1·419 (7)
Cu–S(4)	2·369 (3)	Cl–O(4)	1·380 (9)
S(1)–C(1)	1·706 (9)	S(4)–C(16)	1·708 (8)
C(1)–C(2)	1·40 (1)	C(16)–C(17)	1·40 (1)
C(2)–C(3)	1·34 (2)	C(17)–C(18)	1·37 (1)
C(3)–C(4)	1·40 (2)	C(18)–C(19)	1·39 (1)
C(4)–C(5)	1·33 (2)	C(19)–C(20)	1·35 (2)
C(5)–N(1)	1·36 (1)	C(20)–N(4)	1·36 (1)
N(1)–C(1)	1·36 (1)	N(4)–C(16)	1·36 (1)
S(2)–C(6)	1·710 (12)	S(5)–C(21)	1·694 (10)
C(6)–C(7)	1·42 (1)	C(21)–C(22)	1·41 (1)
C(7)–C(8)	1·35 (2)	C(22)–C(23)	1·35 (2)
C(8)–C(9)	1·38 (2)	C(23)–C(24)	1·41 (1)
C(9)–C(10)	1·37 (2)	C(24)–C(25)	1·35 (1)
C(10)–N(2)	1·39 (2)	C(25)–N(5)	1·36 (1)
N(2)–C(6)	1·35 (1)	N(5)–C(21)	1·36 (1)
S(3)–C(11)	1·707 (11)	S(6)–C(26)	1·671 (11)
C(11)–C(12)	1·40 (1)	C(26)–C(27)	1·41 (2)
C(12)–C(13)	1·39 (2)	C(27)–C(28)	1·33 (2)
C(13)–C(14)	1·39 (2)	C(28)–C(29)	1·41 (2)
C(14)–C(15)	1·36 (2)	C(29)–C(30)	1·37 (2)
C(15)–N(3)	1·34 (2)	C(30)–N(6)	1·36 (2)
N(3)–C(11)	1·35 (1)	N(6)–C(26)	1·37 (2)
N(4)–H(N4)···O(4^{i})	2·889 (9)	Symmetry code	
N(1)–H(N1)···S(3^{i})	3·345 (8)		
N(3)–H(N3)···S(5)	3·216 (7)	(i) $1-x, 1-y, 1-z$	
N(5)–H(N5)···S(3)	3·240 (7)	(ii) $1-x, -y, -z$	
C(30)–H(C30)···O(1)	3·213 (16)	(iii) $-1+x, y, z$	
N(6)–H(N6)···S(6^{ii})	3·215 (8)	(iv) $-x, 1-y, -z$	
N(2)–H(N2)···S(4)	3·268 (9)		
C(27)–H(C27)···O(3^{iii})	3·245 (13)		
C(22)–H(C22)···O(3^{iv})	3·197 (12)		
S(1)–Cu–S(2)	122·0 (1)	S(1)–C(1)–N(1)	117·3 (7)
S(1)–Cu–S(3)	107·5 (1)	S(1)–C(1)–C(2)	127·4 (8)
S(1)–Cu–S(4)	103·9 (1)	C(2)–C(1)–N(1)	115·2 (8)
S(2)–Cu–S(3)	107·1 (1)	C(1)–C(2)–C(3)	121·8 (10)
S(2)–Cu–S(4)	118·8 (1)	C(2)–C(3)–C(4)	120·4 (10)
S(3)–Cu–S(4)	93·3 (1)	C(3)–C(4)–C(5)	118·6 (10)
		C(4)–C(5)–N(1)	120·0 (10)
Cu–S(1)–C(1)	115·1 (3)	C(5)–N(1)–C(1)	123·9 (8)
Cu–S(2)–C(6)	108·8 (4)		
Cu–S(3)–C(11)	101·2 (3)	S(2)–C(6)–N(2)	121·0 (7)
Cu–S(4)–C(16)	107·5 (3)	S(2)–C(6)–C(7)	122·0 (8)
		C(7)–C(6)–N(2)	117·0 (10)
O(1)–Cl–O(2)	108·9 (4)	C(6)–C(7)–C(8)	118·1 (11)
O(1)–Cl–O(3)	108·3 (4)	C(7)–C(8)–C(9)	124·1 (14)
O(1)–Cl–O(4)	110·5 (5)	C(8)–C(9)–C(10)	118·1 (15)
O(2)–Cl–O(3)	109·5 (5)	C(9)–C(10)–N(2)	117·6 (11)
O(2)–Cl–O(4)	110·0 (5)	C(10)–N(2)–C(6)	125·0 (9)
O(3)–Cl–O(4)	109·6 (5)		
S(3)–C(11)–N(3)	119·4 (8)	S(5)–C(21)–N(5)	120·4 (7)
S(3)–C(11)–C(12)	125·0 (7)	S(5)–C(21)–C(22)	124·6 (7)
C(12)–C(11)–N(3)	115·5 (9)	C(22)–C(21)–N(5)	115·0 (9)
C(11)–C(12)–C(13)	120·0 (9)	C(21)–C(22)–C(23)	121·7 (9)
C(12)–C(13)–C(14)	121·0 (11)	C(22)–C(23)–C(24)	120·7 (9)
C(13)–C(14)–C(15)	118·2 (12)	C(23)–C(24)–C(25)	118·3 (10)
C(14)–C(15)–N(3)	119·5 (10)	C(24)–C(25)–N(5)	119·7 (9)
C(15)–N(3)–C(11)	125·7 (9)	C(25)–N(5)–C(21)	124·4 (8)
S(4)–C(16)–N(4)	118·0 (7)	S(6)–C(26)–N(6)	120·2 (8)
S(4)–C(16)–C(17)	125·5 (6)	S(6)–C(26)–C(27)	125·2 (10)
C(17)–C(16)–N(4)	116·5 (7)	C(27)–C(26)–N(6)	114·5 (10)
C(16)–C(17)–C(18)	121·2 (8)	C(26)–C(27)–C(28)	123·1 (12)
C(17)–C(18)–C(19)	120·1 (11)	C(27)–C(28)–C(29)	120·7 (11)
C(18)–C(19)–C(20)	118·1 (9)	C(28)–C(29)–C(30)	117·2 (12)
C(19)–C(20)–N(4)	121·6 (9)	C(29)–C(30)–N(6)	120·6 (12)
C(20)–N(4)–C(16)	122·4 (9)	C(30)–N(6)–C(26)	123·8 (9)

In the perchlorate ion the O—Cl—O angles are very close to the regular tetrahedral value but the Cl—O bond lengths range from 1·380 (9) to 1·436 (6) Å. Their mean value 1·411 (8) Å is comparable with the average distances 1·431 (4) and 1·424 (1) Å found in {bis[2-(2-pyridyl)ethyl] disulfide}copper(I) perchlorate (Warner, Ottersen & Seff, 1974) and in $[CuL_2](ClO_4)_2$, $L = N$-(2-pyridyl)-2-pyrimidylamine (Gouge, Geldard & Sinn, 1980).

The molecular packing is illustrated in Fig. 2. Each $Cu(C_5H_5NS)_4^+$ ion is connected to a perchlorate ion through a hydrogen bond N—H···O, the presence of which is also shown from IR spectra [presence of ν(NH) at 3110 cm^{-1} and absence of ν(SH) at 2500 cm^{-1}]. The cation is also connected to its inversion equivalent through two hydrogen bonds, N—H···S, and to one of the two non-coordinated 2-pyridinethione molecules through another two N—H···S hydrogen bonds (Table 2, Fig. 2). The perchlorate ion is also connected, through a hydrogen bond C—H···O, to the second non-coordinated 2-pyridinethione molecule which, in its turn, is additionally connected to its inversion equivalent (symmetry centre at $1-x, -y, -z$) through two N—H···S hydrogen bonds. It is worth noting that O(3) is approached at hydrogen-bond distance by two H atoms (Table 2). Hydrogen bonding is, obviously, important both for packing and for determining the orientation of the 2-pyridinethione ligands and the non-coordinated molecules.

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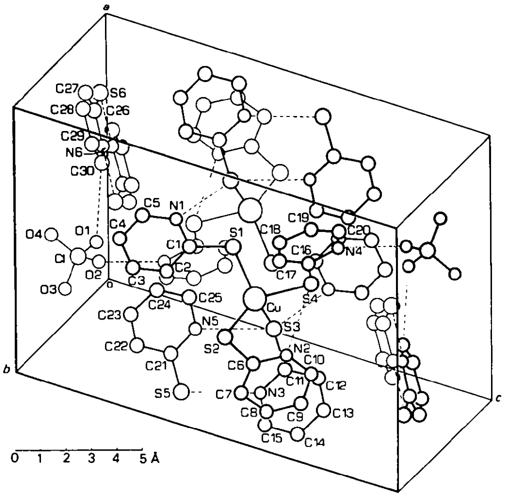

Fig. 2. Clinographic projection of TPTCP showing the molecular packing in the unit cell.

References

BATTAGLIA, L. P., CORRADI, A. B., NARDELLI, M. & VIDONI TANI, M. E. (1976). *J. Chem. Soc. Dalton Trans.* pp. 143–146.

COTTON, F. A., FANWICK, P. E. & FITCH, J. W. (1978). *Inorg. Chem.* **17**, 3254–3257.

EVANS, I. P. & WILKINSON, G. (1974). *J. Chem. Soc. Dalton Trans.* pp. 946–951.

FLETCHER, S. R. & SKAPSKI, A. C. (1972). *J. Chem. Soc. Dalton Trans.* pp. 635–639.

GOUGE, E. M., GELDARD, J. F. & SINN, E. (1980). *Inorg. Chem.* **19**, 3356–3359.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71–151. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

KOKKOU, S. C., FORTIER, S., RENTZEPERIS, P. J. & KARAGIANNIDIS, P. (1983). *Acta Cryst.* C**39**, 178–180.

MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J.-P. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain-la-Neuve, Belgium.

OKAYA, Y. & KNOBLER, C. B. (1964). *Acta Cryst.* **17**, 928–930.

PAULING, L. (1960). In *The Nature of the Chemical Bond,* 3rd ed. Ithaca: Cornell Univ. Press.

STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

WARNER, L. G., OTTERSEN, T. & SEFF, K. (1974). *Inorg. Chem.* **13**, 2819–2826.

Acta Cryst. (1985). C**41**, 1043–1045

A Linked Diphosphido Ironcarbonyl Complex, μ-*P*,*P*′-Diphenyltrimethylenebis(phosphido)-μ-*P*:μ-*P*′-bis(tricarbonyliron)(*Fe–Fe*), $[Fe_2(C_{15}H_{16}P_2)(CO)_6]$

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Abstract. $M_r = 537{\cdot}99$, monoclinic, $P2_1/n$, $a = 11{\cdot}551\,(3)$, $b = 13{\cdot}254\,(3)$, $c = 15{\cdot}655\,(5)$ Å, $\beta = 106{\cdot}28\,(2)°$, $U = 2300{\cdot}6\,(9)$ Å^3, $Z = 4$, $D_x = 1{\cdot}55$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 14{\cdot}7$ cm^{-1}, $F(000) = 1088$, $T = 292$ K, $R = 0{\cdot}035$ for 2576 observed reflections. The tetragonal-pyramidal metal-atom coordination geometries are joined along a basal edge formed by the mutually bridging phosphorus termini of the $PhP(CH_2)_3PPh$ group. The 'non-bonding' P(1)···P(2) distance is short, 2·742 (1) Å, suggesting some interaction.

Introduction. Diphosphido-bridged diiron carbonyl complexes, $[Fe_2(CO)_6(\mu\text{-}R_2P)_2]$, have recently been extensively studied as potential dinuclear, homogeneous catalysts (Ginsburg, Rothrock, Finke, Collman & Dahl, 1979; MacLaughlin, Carty & Taylor, 1982; Fultz, Rheingold, Kreter & Meek, 1983). We have recently reported the structures of two members of this class of compounds containing phosphido groups linked by an all-phosphorus bridge $[Fe_2(CO)_6(PR)_4]$, $R = CH_3$ (4) or C_6H_5 (5) (Rheingold & Fountain, 1984). We now report the structure of an all-carbon-linked diphosphido complex $[Fe_2(CO)_6\{C_6H_5P(CH_2)_3PC_6H_5\}]$, (1).

Experimental. Crystals (Flood, DiSanti & Campbell, 1978) obtained from acetone recrystallization. Yellow-orange, 0·26 × 0·30 × 0·35 mm, mounted on glass fiber. Nicolet *R*3, graphite monochromator, unit cell from least-squares fit of angular settings of 25 reflections ($19 \le 2\theta \le 24°$). 3306 reflections, $2\theta \le 45°$, collected for $-11 \le h \le 11$, $0 \le k \le 14$, $0 \le l \le 16$ at 3° min^{-1} using $\theta/2\theta$ scans. No decay in three standard reflections, semi-empirical absorption correction (transmission 0·67 to 0·83) based on ψ-scan measurements of six reflections at different azimuthal angles (10° increments). 2576 unique observed reflections $[F_o \ge 3\sigma(F_o)]$, $R_{\rm int} = 0{\cdot}021$. Multisolution direct methods (*SOLV*), blocked-cascade least squares on *F*, $w^{-1} = \sigma^2(F) + 0{\cdot}0001\,F^2$, complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). Non-hydrogen atoms anisotropic, hydrogen atoms fixed, idealized contributions, C—H = 0·96 Å, $U({\rm H}) = 1{\cdot}2U_{\rm eq}({\rm C})$, extinction correction necessary, $F = F_o/[1{\cdot}0 + (2{\cdot}1 \times 10^{-5})F^2/\sin(2\theta)]^{0{\cdot}25}$. 281 parameters, $R = 0{\cdot}035$, $wR = 0{\cdot}032$, slope of normal probability plot = 1·30, max. final $\Delta/\sigma = 0{\cdot}09$, largest peak in final difference map = 0·23 e Å^{-3}, deepest trough = 0·25 e Å^{-3}. *SHELXTL* program system (Sheldrick, 1984).

Discussion. Atomic coordinates are given in Table 1, bond lengths and angles in Table 2.* The molecular

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* Lists of structure factors, anisotropic thermal parameters and hydrogen-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42153 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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